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INVESTIGATION ON THERMODYNAMIC ASPECTS FOR MICELLIZATION AND SURFACE ACTIVE PROPERTIES OF PYRIDINIUM SURFACTANTS

SYNOPSIS

Submitted in partial fulfilment of the Requirements for the award of the degree of Ph.D.

Submitted by

Ravi Kant
Enrollment No.: H14837

Under the supervision of

Prof. (Dr.) Yogesh Kumar Walia

DEPARTMENT OF CHEMISTRY
SCHOOL OF BASIC AND APPLIED SCIENCES
CAREER POINT UNIVERSITY HAMIRPUR
TIKKER (KHARWARIAN), BHORANJ
HAMIRPUR (HP)-176041, INDIA

Academic Session

2022-2023

INTRODUCTION

Surfactants are amphiphilic molecules having great potential to lower the surface tension of the water and most important compounds in our daily needs. These are mainly used in washing powder, clothing cleanser, washing adhesive, clothing pills, house cleansing, detergents, floor cleaner, apparatuses cleaning, disinfectants and sanitizers etc. The usage and applications surfactants are expanding day by day (Altenbaher et al., 2014).

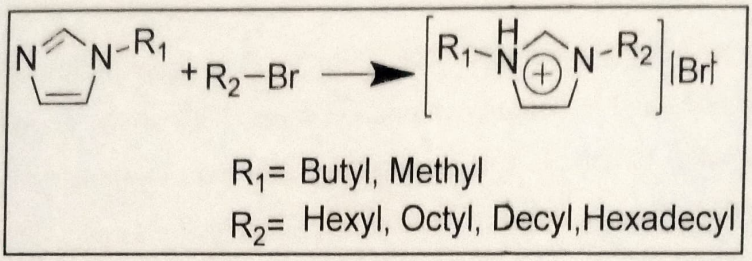
Surfactants due to amphiphilc nature, contain both hydrophobic tails (water insoluble) and hydrophilic head groups (water soluble); the tails comprise of hydrocarbon chains. Surfactants are generally classified into four categories viz. anionic, cationic, zwitter ionic and non-ionic surfactant Out of the four categories, the cationic surfactants obtain numerous industrialized applications and compose nearly 7% of the total industrialized surfactant showcase prospective (Samiey et al., 2014).

Cationic surfactants are also attaining importance in the preparation of liposomes, softeners, cosmetic products, electrode coating and the stabilization of epoxy resin polymer latexes as well as in removal and manufacturing (Song & Rosen, 1996).

Six membered pyridine based surfactants are typically cationic surfactants and has been synthesized with an n-alkyl halide and pyridine and further halide ion has been substituted by p-toluenesulfonate group by means of a double substitution reaction, to study electrochemical behavior cyclic voltammetry (Lara-Hernández et al., 2021). These pyridine-based surfactantshave shown good thermal stability, micellization and surface tension lowering properties (Patial et al., 2014). Ester functioned pyridinium ionic liquids, a class of cationic surfactant have proven as a good candidate for antimicrobial activity (Trush et al., 2019). Glycerol substituted pyridine surface exhibit improved surface-active properties, binding with DNA and low toxicity as compared with commercially available cationic surfactants like cetyl pyridinium bromide and tetradecyl trimethyl ammonium bromide (Singh et al., 2009)

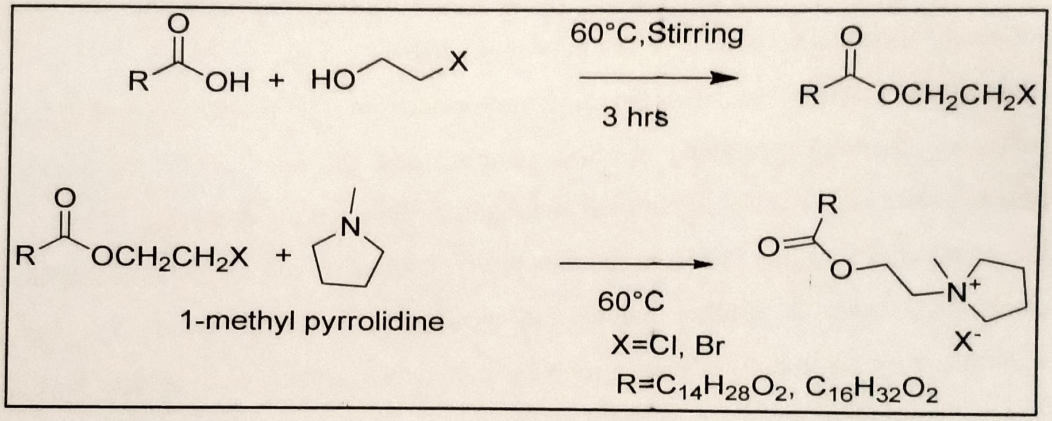
LITERATURE REVIEW

Baltazar et al., (2007) synthesized asymmetrical monomeric cationic liquids by mixing of 1-alkylimidazole with the corresponding 1-bromoalkane, the reaction mixture was refluxed at 70°C with continuous stirring for 24 hrs in presence of isopropanol as solvent medium (Scheme 1).



Scheme 1

Patial & Chandel (2009) studied that the linear fatty acids on reaction with chloro/bromo ethanol in the occurrence of catalytic quantity of sulphuric acid below solvent-free conditions were transformed into particular esters which on reaction through 1-methylpyrrolidine give ester-functionalized pyrrolidinium surfactants (Scheme 2).

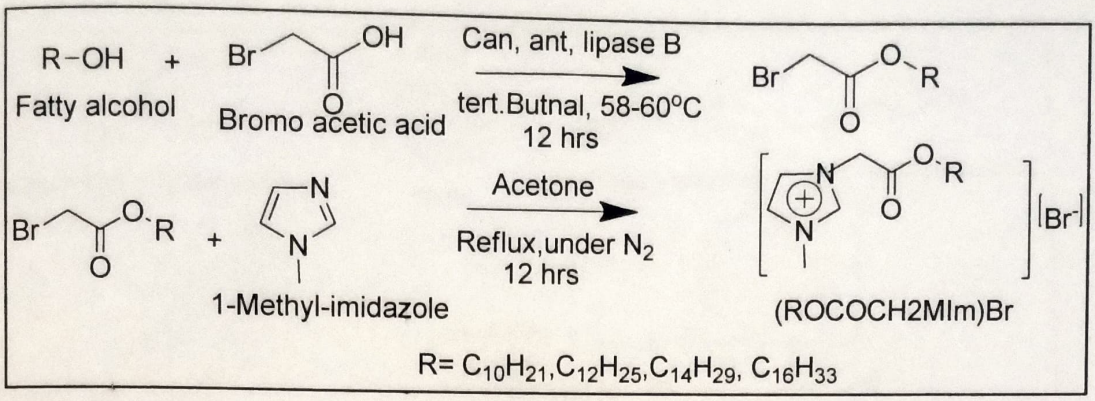


Scheme 2

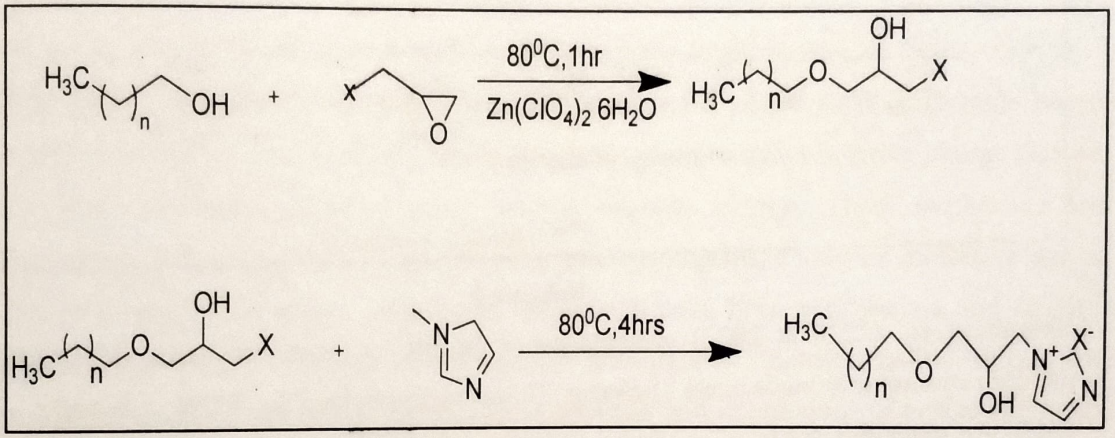
Kanjilal et al., (2009) synthesized (Scheme 3) methyl-imidazolium surfactants of different chain length and studied their micellization and antimicrobial activities. The results have revealed that these compounds possess good activities against selected strains.

Chauhan et al., (2012) reported the synthesis of some cationic surfactants by reacting fatty alcohols with epichlorohydrin in the presence of zinc perchlorate hexahydrate at 80°C for 1 hour resulting in the formation of β –hydroxy-ϒ-alkoxyl bromo ethers which on further with N-methylimidazole at 80°C for 4 hours furnishing the desired cationic surfactants (Scheme 4).

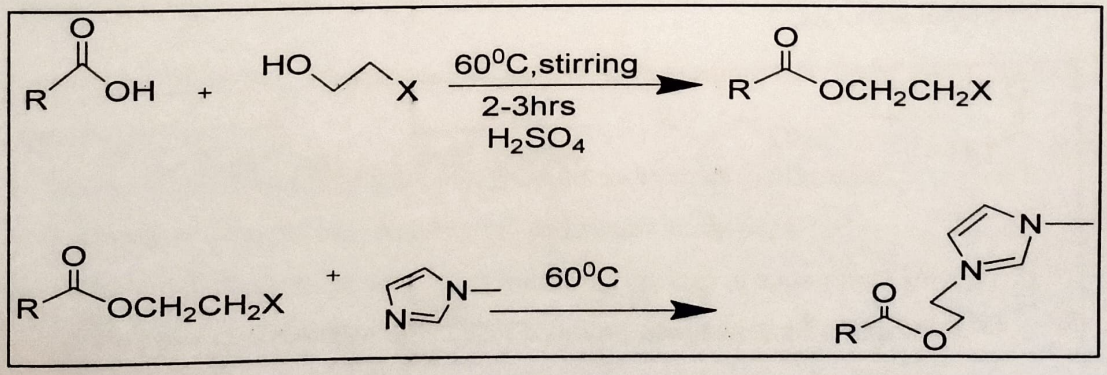
Ahmad et al., (2013) reported ester based cationic surfactants. Fatty acids were made to react with halogenated alcohols and catalytic amount of sulphuric acid were added at 60°C for 3hrs with stirring, furnishing with 1-methyl imidazole at 60°C gives imidazolium based monomeric surfactants (Scheme 5).



Scheme 3

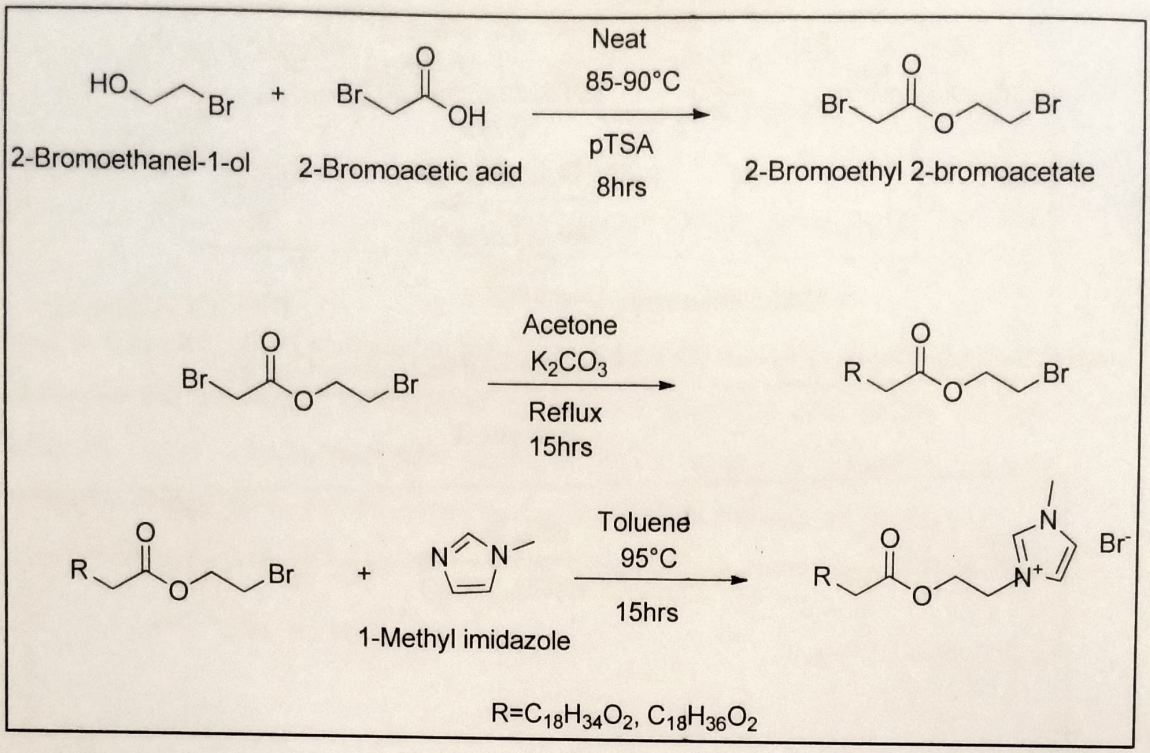


Scheme 4



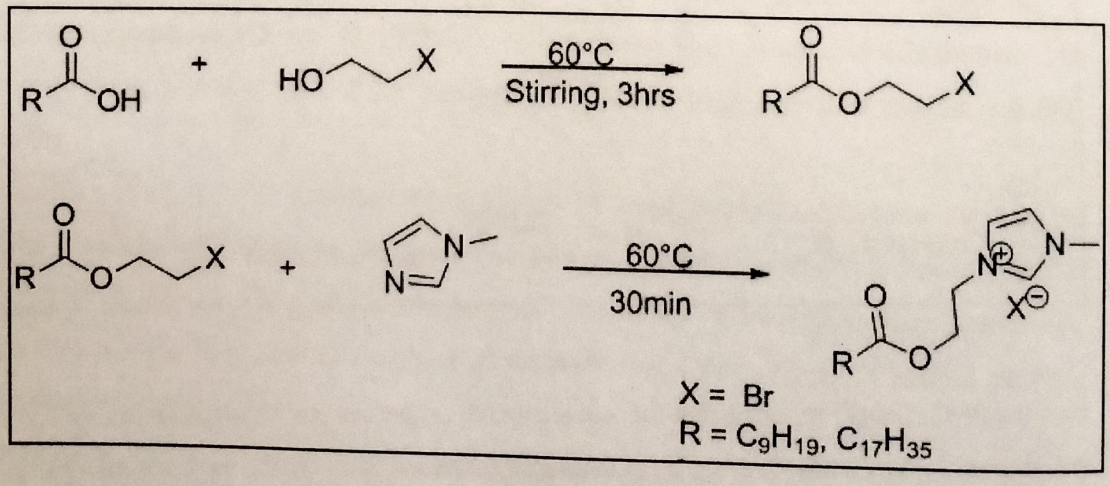
Scheme 5

Bhadani et al., (2017) reported that the surface active properties and biodegradation speed of the renewable raw surfactants is depend upon the environment of the hydrophobic group. Renewable ester functionalized oleic and stearic acid based imidazolium surfactants could be manufactured (Scheme 6) and characterized by using spectroscopic methods. The new surfactants were investigated for their self aggregation properties and biodegradability in aqueous solution.



Scheme 6

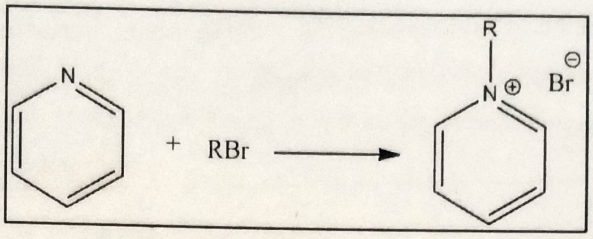
Sharma et al., (2020 & 2023) synthesized renewable raw material-based imidazolium cationic monomeric surfactants (Scheme 7) and characterized by FTIR, 1H NMR and TGA. An extensive study of synthesized compounds in ethanol has indicated that there were significant integrations between surfactants and ethanol molecules and shown good antimicrobial activities.



Scheme 7

Marek et al., (2010) synthesized quaternary pyridinium salts of different alkyl chains and proposed HPLC technique for synthesis & detection of these compounds in laboratory

and semi-industrial scale. The preparation method of these alkyl pyridinium quaternary salts has been depicted in scheme 8.



Scheme 8

RESEARCH GAP IDENTIFICATION

Several applications of cationic surfactants have been found in various fields whether it is academic or industrial. Pyridinium surfactants are the major class of cationic based amphoteric surfactants in which hydrophilic head group contain positive charge and on the other hand, hydrophobic group contain negative charge. These surfactants are frequently used as surface tension lowering, antiseptic agents, corrosion inhibitors and in cosmetics etc. Since a few pyridinium surfactants have been synthesized and studied their various physical parametersbut detailed investigation, thermodynamic aspects for micellizationor self-assembly, conductance behavior and interactions of surfactants with solvent molecules were found scanty.

OBJECTIVES

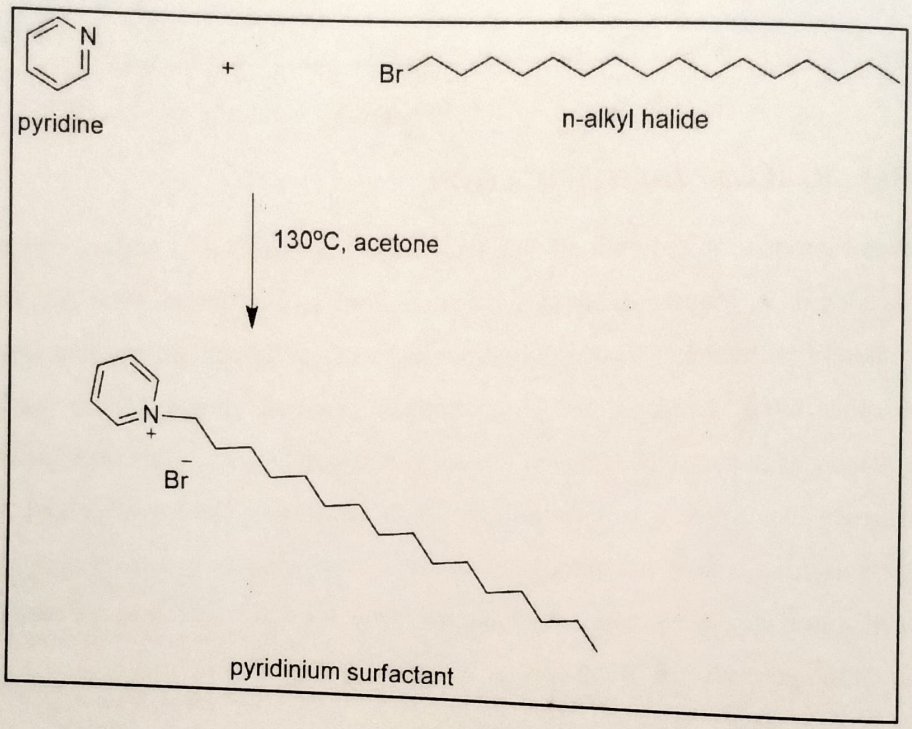
Keeping in view the above points, present investigation has been taken with the following objectives:

- Synthesis and characterization ofpyridinium monomeric surfactants.
- Estimation of the thermal stability of synthesized surfactants.
- Study conductance behavior of pyridinium surfactants in appropriate solvent.
- Evaluation of interfacial properties of solutions of synthesized compounds.
- Assessment of the thermodynamic behavior for micellization in solutions.

PROPOSED METHODOLOGY

Synthesis of pyridinium based monomeric surfactants: The calculated amount of pyridine and n-alkyl halide will be mixed in RB flask, acetone would be used as solvent for the reaction medium (Scheme 9). The reaction would stirred at high temperature of 120°C approx. for 4 hours. The reaction would be monitored by using TLC plates coated with Silica Gel G in transportable medium (hexane and ethyl

acetate in 9:1). Filters off the precipitates formed using Whatman filter paper and cold acetone to be added for recrystallization. The purity of the compound formed would be detected by checking its melting point. Furthermore, the purity of the synthesized compound to be confirmed by using 1H NMR, 13C NMR and FTIR spectroscopies.



Scheme 9

Measurements:

^{1}HNMR: ^{1}HNMR spectrums would be obtained from AMRC, IIT Mandi, Model "JNM ECX-500" at 500Mz by using $CDCl_3$ as solvent at ambient temperature to determine the presence of proton on hydrophobic chains and on the pyridine backbone.

^{13}CNMR: ^{13}CNMR spectrums would be outsourced from AMRC, IIT Mandi, Model "JNM ECX-500" using $CDCl_3$ as solvent at ambient temperature to determine the carbon atoms present in molecular structure of the synthesized compounds.

FTIR: FTIR spectrum outsourced from AMRC, IIT Mandi, Model "K8002AA carry 660 FTIR" with KBr technique in range of 4000-400 cm^{-1}, to check the product formation.

Thermo gravimetric Analysis (TGA): Thermo gravimetric Analysis (TGA) would be outsourced at constant rate of heating (20°C/min.) on Perkin Elmer STA 6000 from SAIF-STIC Cochin.

Conductivity Measurements: Freshly prepared standard solutions of KCl solution will be used for the calibration of conductometer. The conductivity of aqueous solutions of synthesized surfactants would be measured at four different temperatures with "HANNA H12300 Microprocessor conductivity meter" and a dropping type conductivity cell with Platinum electrode. The specific conductance and molar conductance would measure in μS and μSm-1mol-1 respectively.

Density and Viscosity Measurements: The viscosity of each synthesized pyridinium monomeric surfactant will be measured with Ostwald's type viscometer at 298K using water as solvent. The viscosity would be calculated by using the expression:

$$\eta_1/\eta_2 = \rho_1 t_1 / \rho_2 t_2$$

Here η_1, η_2, ρ_1, ρ_2, t_1 and t_2 is the viscosity, density and time of flow for known solution and pure solvent, respectively. The densityof surfactant solution would be measured using specific gravity bottle. The density and viscosity were calculated in g/cm3 and Pa.s, respectively.

Surface Active Properties: Surface tension for the aqueous solutions of synthesized surfactants at air/water interface would be measured with stalagmometer by using the drop number method at 298K.. Surface tension parameters i.e. surface excess concentration (Γ_{CMC}), minimum surface area occupied at air/water interface (A_{min}), effectiveness of surface tension reduction (γ_{min}) and CMC would be calculated from slope of surface tension vs. concentration of surfactant solution. The surface tension of the solutions will be calculated by using the expression:

$$\gamma_1 = \eta_o d_1 / \eta_1 d_o \times \gamma_o$$

Here η_o, η_1, ρ_o, ρ_1, γ_o and γ_1 are the viscosity, density and surface tension for pure solvent and known solution, respectively.

THESIS OUTLINE

Thesis will comprise five chapters as:

Chapter I (Introduction) includes the discussion of use & applications of surfactants; synthesis, characterization & various properties of cationic surfactants.

Chapter II (Literature Review) gives detailed review of published literature with reference to synthetic techniques, physiochemical behavior, electrical conductance and thermodynamic aspects of micellization of various surfactants.

Chapter III (Materials and Methods) includes the required materials and methodology adopted for carrying out the present investigation. Material, methodsand reaction procedures usedwould be described in detail.

Chapter IV (Results and Discussion) includes the detailed results obtained from present studies. Results regarding yield, melting point of synthesizedpyridinium surfactants along with characterizations would be presented in this chapter. Some important properties would be estimated from different techniques to estimate thermal stability, micellization, interactions with solvent and surface tension lowering properties of synthesized surfactants.

Chapter V (Conclusion and Recommendations) includes brief and concise summary of the results. It suggested the needof such unexplored studies. It also illustrates the scope of further researchbased on results and findings.

Chapter VI (References) Harvard referencing style will be followed for references writing and citation.

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Ravi Kant
PhD Research Scholar
UID No: H14837

CERTIFICATE
(SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the Synopsis titled, **"Investigation on Thermodynamic Aspects for Micellization and Surface Active Properties of Pyridinium Surfactants"**, submitted by **Mr. Ravi Kant** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the **Department of Chemistry, School of Basic and Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 17/06/23.

05/07/2023

Dr. Yogesh Kumar Walia, Professor, Department of Chemistry, Career Point University, Hamirpur (H.P.) – 176041, India

(Supervisor)

Research Advisory Committee

Dr. Kamal Kishore, Associate Professor, Department of Chemistry, Eternal University, Baru Sahib, Solan, H.P. **(Co-Supervisor)**

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(RAC Member)

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(RAC Member)

05/07/2023

Dr. Y.K. Walia, Professor, CPU, Hamirpur (H.P.)

(Head, Department of Chemistry)

05.07.2023

Dr. Kuldeep Kumar, Associate Professor, CPU, Hamirpur (H.P.)

(Dean R & D)